Modification of surface energy and wetting of textile fibers

Chapter 6

Modification of Surface Energy and Wetting of Textile Fibers

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Additional information is available at the end of the chapter

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Abstract

The modification of the surface energy of textile fibers to improve functional properties such as the wettability was reviewed. This modification can be achieved by physical or chemical methods or by the combination of both. Applications of plasma treatment to improve the wettability of natural and synthetic fibers were considered and some methods of wettability measurement were mentioned. Subsequently the methods aimed to confer water and oil repellency were discussed and the treatment by UV curing of fluorochemicals was explained in detail. Finally the sol-gel techniques useful to modify the surface properties of textiles were introduced and the results of water and oil repellency achievable by sol-gel were presented.

Keywords: Surface energy, Wetting, Textile fibers, Plasma, Contact angle, Water repellency, Oil repellency, Fluorochemicals, UV-curing, Sol-gel

1. Introduction

The modification of the surface energy of textile fibers is pursued with the aim of improving their own hydrophilicity, wettability, and dyeability or of conferring functional properties such as hydro and oil repellency, soil release, adhesion improvement, and antistatic performances. If the modification is confined to a thin surface layer of the fibers, the bulk properties of a textile material, such as mechanical strength, flexibility, breathability, and softness, should not be compromised.

The wettability of a surface depends on the surface tension of the liquid that goes into contact with the same. Water has a very high surface tension (72.8 mN/m), so it tends to wet only surfaces bearing highly polar groups; otherwise, it forms spherical drops with contact angles higher than 90°. Instead, apolar liquids of lower surface tension get drops flatter than those of water. Hydrophobic or oleophobic surfaces are difficult to wet by water or apolar liquids, respectively, and are called low-energy surfaces. Wetting, in reality, is much more complex than as described by classical laws. This primarily comes from the non-ideality of solid substrates that are both rough and chemically heterogeneous [1]. Such a situation commonly occurs in the case of textile materials and can be evidenced by the hysteresis of the contact angle [2].

The surface modification of textile fibers can be achieved by physical or chemical methods or by the combination of both. Plasma treatments and exposure to radiations are mainly representative of physical methods, although their effects are often accomplished in the presence of reactive gases or after impregnation with suitable chemicals. However, chemical treatments can generally be carried out with oxidants or other finishing agents, followed by thermal treatment. Among the latter methods, sol–gel techniques are the more promising for surface modification.

Among the textile fibers, there are many differences regarding wettability and surface structure. Natural fibers have cellular structures that are more complex than those of man-made fibers obtained by chemical spinning. Wool and fine animal fibers are mainly composed of keratin, but show the structure of composite material formed by an assembly of cuticle cells in the form of scales and cortical cells surrounded by a keratin cell membrane and held together by an intercellular cement. The cell membrane consists of a chemically resistant protein layer and a lipidic layer that constitutes a hydrophobic barrier to the transfer of water and dye molecules from an aqueous solution [3]. Therefore, a wettability improvement of these fibers can be obtained by the removal of the hydrophobic lipidic layer and by the introduction of polar groups on the surface, both performed by chemical and/or physical means. A chemical treatment is usually made by chlorination, which modifies the scale edges of wool and increases the critical surface tension of the fibers. In such a manner, the chlorinated fibers are made more wettable and dyeable and can be coated with polymers, conferring the shrink-resist effect. However, many research works are carried out to find alternative processes that avoid chlorination in order to remove the problem of the formation of absorbable organohalogen compounds in wastewaters [4]. To this aim, plasma treatments have extensively been studied, but even other cheaper eco-friendly processes have been experimented, in particular for dyeability improvement, such as treatment with enzymes or ultraviolet (UV) irradiation. A list of selected references is reported in Table 1.

Cotton and cellulose fibers are more homogeneous than wool and are richer in hydroxyl groups ththat confer higher hydrophilicity; hence, their surface modifications are mainly directed to confer hydro and oil repellency. This topic will be treated in paragraphs 3 and 4. Moreover, the exhaust dyeing of cotton with anionic dyes, i.e., direct and reactive, request a high concentration of electrolytes in dyebath to reduce negative charges on the fiber surface and to promote the exhaustion of dyes. This requirement creates environmental issues due to the removal of high concentrations of salts and dyes from wastewaters. To overcome such

Process type	Topic	Reference
LPP	Surface characterization	Kan 2004 [5]
LPP	Surface composition	Kan 2005 [6]
LPP	Review	Kan 2007a [7]
LPP	Effect on wool dyeing	Kan 2007b [8]
APP	Wettability improvement	Wang 2007 [9]
LPP	Application of HMDSO coating	Rombaldoni 2008 [10]
LPP	Characterization of wool coated	Rombaldoni 2009 [11]
APP	Ageing effect	Naebe 2011 [12]
Enzyme	Effect on dyeing kinetics	Riva 2002 [13]
Enzyme	Effect on wool dyeing	Onar 2005 [14]
Enzyme	Dyeability, antifelting	Cardamone 2006 [15]
Enzyme	Effect on wool dyeing	Parvinzadeh 2007 [16]
Enzyme	Effect on wool dyeing	Cui 2009 [17]
Enzyme	Low temperature dyeing	Periolatto 2010 [18]
Enzyme	Influence on dyeing	Periolatto 2011 [19]
Enzyme	Influence of lipids on dyeing	Ferrero 2015 [3]
UV irradiation	Printability improvement	Shao 2001 [20]
UV irradiation	Surface modification, dyeing	Xin 2002 [21]
UV irradiation	Improving properties	El-Zaher 2002 [22]
UV irradiation	Dyeability improvement	Micheal 2003 [23]
UV irradiation	Multifunctional finishing	Periolatto 2013 [24]
UV irradiation	Differential dyeing	Migliavacca 2014 [25]
UV irradiation	Low temperature dyeing	Periolatto 2014 [26]

APP: Atmospheric pressure plasma; LPP: low-pressure plasma.

Table 1. Processes of wool surface modifications.

problems, many treatments with plasma, chemicals, and polymers were experimented to impart a cationic character to the cotton fiber surface [27]. Chitosan, 2-amino-2-deoxy-(1 → 4)-β-D-glucopyranan, derived from the deacetylation of the chitin component of the shells of crustaceans, is undoubtedly one of the more promising multifunctional polymers for surface modification of textiles [28]. It is a biopolymer with unique properties such as biodegradability, nontoxicity, and antimicrobial activity; hence, it was mainly applied to textiles as an antimicrobial finishing agent. Moreover, cotton treated with chitosan shows improved absorption of anionic dyes due to electrostatic attraction arising from the cationized amino groups of

chitosan in an acidic medium. However, chitosan should stably be bonded to the fiber surface to ensure the fastness of treatment to washing. To this aim, crosslinking agents such as dialdehydes are used, although these are toxic chemicals. On the contrary, an eco-friendly grafting of chitosan onto cotton can be carried out by radical UV curing in the presence of a low concentration of a photoinitiator [29, 30].

A list of selected references on the surface modification of cotton and cellulose fibers is reported in Table 2, whereas a recent review was published by Kalia et al. [31].

Process type	Topic	Reference
LPP, APP	Penetration into textile structures	Poll 2001 [32]
LPP	Dyeability of fabrics	Ozdogan 2002 [33]
LPP	Repellent coating	Allan 2002 [34]
LPP	Fluorination	McCord 2003 [35]
APP	Bleaching and dyeing	Prabaharan 2005 [36]
APP	Hydrophobic coating	Kim 2006 [37]
APP	Dyeability of fabrics by acid dyes	Karahan 2008 [38]
LPP	Hydrophilicity improvement	Pandiyaraj 2008 [39]
LPP	Dyeability of Tencel	Mak 2006 [40]
Chitosan	Crosslinking for antimicrobial cotton	El-tahlawy 2005 [41]
Chitosan	Crosslinking on UV-irradiated fibers	Alonso 2009 [42]
Chitosan	UV curing for antimicrobial textiles	Ferrero 2012 [29]
Chitosan	UV curing for antimicrobial textiles	Periolatto 2012 [30]
Chitosan	UV curing for antimicrobial cotton	Ferrero 2013 [43]

APP: atmospheric pressure plasma; LPP: low-pressure plasma.

Table 2. Processes of surface modifications of cotton and cellulose fibers.

Synthetic fibers such as polyamide and polyester have a compact structure with a low content of polar groups, whereas polypropylene is lacking of them; these are substantially hydrophobic and can be subjected to surface etching by plasma and oxidation to increase porosity and wettability, but the latter purpose is often pursued by grafting of polar monomers or application of hydrophilic coating.

In a similar manner, hydrophobicity and oleophobicity can be increased with a suitable coating obtained by plasma. A selection of articles published in the last 15 years is reported in Table 3.

Fiber	Plasma	Topic	Reference
PET	LPP	Surface modification by silane	Negulescu 2000 [44]
Cotton, PET, silk	LPP	Surface modification by air	Riccardi 2001 [45]
PET	LPP	Surface modification by SF_6	Riccardi 2003 [46]
PET	LPP	Wettability and dyeability by SF_6	Barni 2005 [47]
PET, PA	LPP	Surface modification by acrylic acid	Cireli 2007 [48]
PET	LPP	Hydrophilicity by O_2 and NH_3	Calvimontes 2011 [49]
PET	APP	Penetration depth of modification	Wang 2008 [50]
PET	APP	Fluorocarbon nano-coating	Leroux 2008 [51]
PET	APP	Surface oxidation and silicon resin	Leroux 2009 [52]
Cotton, PET, PA	APP	Water and oil absorbency	Samanta 2009 [53]
PET, PA	APP	Antistatic effect	Samanta 2010 [54]
PET	APP	Surface modification	Gotoh 2010 [55]
Acrylic	LPP	Hydrorepellent coating	Pane 2001 [56]
Acrylic	APP	Water and oil repellency	Ceria 2010 [57]
PET, acrylic	LPP	Wettability by capillary rise	Ferrero 2003 [58]
PET, PA, PP	LPP	Dyeability by acrylic acid	Ferrero 2004 [59]
PP	LPP	Wettability by CF_4	Kwon 2002 [60]
PP	APP	Surface treatment of nonwoven fabrics	Väänänen 2010 [61]

APP: Atmospheric pressure plasma; LPP: low-pressure plasma; PA: polyamide; PET: polyethylene terephtalate; PP: polypropylene.

Table 3. Selected articles on the surface modification of synthetic fibers by plasma treatment.

2. Wettability by plasma treatments

Plasma is commonly defined as an ionized gas in a neutral state with an equal density of positive and negative charges. It is often referred to as the "fourth state of matter," which can be reached in a wide range of temperatures and pressures. From a chemical point of view, plasma mostly consists of a mix of activated gaseous particles comprising free electrons, radicals, ions, UV radiations, and various highly excited neutral and charged species. It is considered to be a very interesting medium for material processing technologies, with particular regard to surface engineering. In fact, a large variety of treatments aimed at surface modification of different substrates can be carried out, including etching, cleaning, activation, and coating, as detailed below:

- *Etching*: the removal of the bulk substrate material, occurs when the interaction between the solid surface and plasma generates gaseous byproducts, including atoms or molecules, carried away from the surface substrate, removing minimal fractions of bulk material.

- *Cleaning*: the removal of contamination in the form of etching, but with very high selectivity. Only the unwanted surface contaminant is volatilized and removed, whereas the substrate remains unaffected by the process.
- *Activation*: the enhancement of the substrate energy, which generates chemically reactive sites on a previously nonreactive surface.
- *Coating*: the deposition of a functional thin film, occurs if the plasma–solid surface interaction creates a solid-phase material. This process is sometimes called plasma enhanced chemical vapor deposition or plasma polymerization.

Plasmas can be classified by taking into account the employed generation technology (power supply and pressure range) into two major categories: thermal plasmas (very high temperature, not suitable for heat-sensitive materials) and non-thermal plasmas (close to room temperature and suitable for treating textiles). Non-thermal plasmas are also known as low-temperature plasmas and can be subdivided into many different technologies considering the electrical power supply, the operating pressure (low or atmospheric), and the geometrical arrangements.

The laws of plasma physics would make it easier to generate large-volume plasmas at reduced pressure rather than at atmospheric pressure. Moreover, in a closed system under low pressure, it is easier to control the characteristics and composition of the gas atmosphere from which the plasma is generated and, hence, the process chemistry rather than in a system at atmospheric pressure open to ambient air. Nevertheless, a closed system is not easily adaptable to a continuous process of fabric treatment. Therefore, although most of the plasma applications on polymeric materials, including textiles, have been studied using low-pressure plasma (LPP), the atmospheric pressure plasma (APP) technique has demonstrated to be the most interesting tool for large-scale applications on textiles.

Plasma treatments are able to modify the fiber surface, leaving the bulk properties unaffected, and this characteristic is very important for the modification of textile fibers that should not lose their mechanical and chemical properties after treatment. Moreover, the finishing of textile fabrics by plasma technologies can advantageously replace some wet chemical applications as environmental friendly processes, since they do not require water and a high amount of chemicals. By controlling the plasma variables, such as the nature of gas, discharge power, pressure, and exposure time, a great variety of surface properties can be improved, mainly cleaning, wettability, hydrophobic and oleophobic properties, soil release, adhesion of coatings, dyeability, printability, and flame resistance.

An exhaustive book on the applications of plasma technologies to textiles was published by Shishoo [62], whereas the surface modifications by plasma treatments were reviewed by Radu et al. [63] and Morent et al. [64]. Reviews on atmospheric plasma treatments were published by Kale et al. [65] and, more recently, by Wolf [66]. In particular, the plasma pre-treatments to improve dyeability were considered by Deshmukh and Bhat [67], whereas Hossain and Hegemann studied the deposition of thin coatings on synthetic fibers to confer a substrate independent dyeability [68].

The modification induced by plasma treatment on a polymeric surface as a film is easily measured by contact angle determination with the sessile drop method. In the case of textile materials, instead, the measure is strongly affected by the heterogeneous surface structure; therefore, the porosity of the fabrics can often determine a suction effect on the water drop, preventing the contact angle determination. Another technique consists of weight variation measurement by a Wilhelmy balance during capillary wicking. The variety of techniques commonly used to measure contact angles has recently been highlighted by Yuan et al. [69].

Moreover, the hydrophilicity of plasma-treated fabrics can be tested according to the BS 4554:1970 method, known as the drop test, in which a drop of 100.0 μL of deionized water is placed on the surface of the specimen. The time required for the droplet to completely penetrate the fabric was measured by means of a stopwatch.

Poll et al. [32] measured the hydrophilization effect induced by plasma through the suction test. A capillary is filled with a colored test liquid and positioned onto the surface of the fabric layer to be checked. The liquid is absorbed by the fabric to form a colored circle. The diameter of the circle formed after an exposure time of 20 s is a measure of the hydrophilization effect.

Another wettability test can be performed on a fabric strip that is kept vertical, with the lower end immersed in water–dye liquor. A spontaneous wicking occurs due to capillary forces. The absorption height h is recorded as a function of time, and the absorption rate is calculated (capillary rise method, as shown in Figure 1; reprinted with the kind permission of the author in [70]).

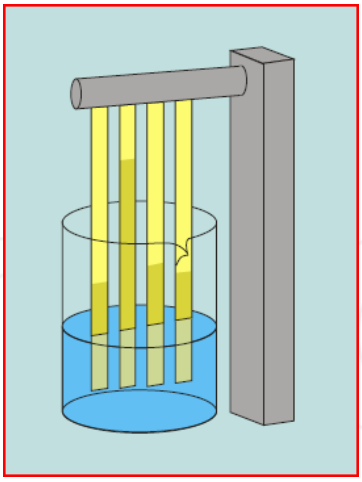

Figure 1. Capillary rise method.

Ferrero [58] applied this method to the wettability measurements on plasma-treated synthetic fabrics (polyester and acrylic). The processing of capillary rise data proposed in this work allowed the assessment of wettability improvement by plasma treatment carried out in

different gases (nitrogen, air, and oxygen). Wettability is strongly enhanced by plasma treatment, and after some time, the height reaches an equilibrium value h_{eq}, as shown, for example, in Figure 2, where the wicking curves of untreated and plasma-treated PETs are compared. It is evident that wettability is strongly improved by a mild nitrogen plasma treatment (25 W, 30 s, 65-Pa pressure in a Plasmod apparatus).

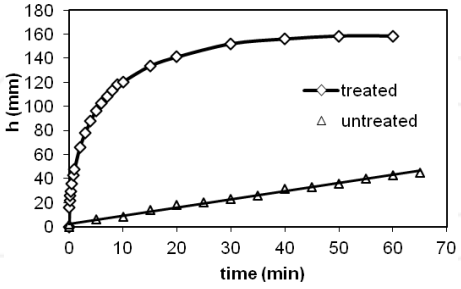

Figure 2. Comparison between the wicking curves of untreated and plasma-treated PET fabrics.

The maximum equilibrium height h_{eq} can be related to the equilibrium static contact angle θ_{eq}, generally smaller than the dynamic one, by equation (1):

$$h_{eq} = \frac{2\gamma \cos\theta_{eq}}{\rho g R_S} \tag{1}$$

where γ and ρ are the surface tension and density of the liquid, respectively, R_S is the mean static radius of pores, and g is the gravity acceleration. In the early stages of the process, the hydrostatic pressure in equation (1) can be neglected; hence, h can be related to θ, advancing contact angle of the liquid on the solid, by Washburn's equation (2):

$$h^2 = \frac{r\gamma \cos\theta}{2\eta} t \tag{2}$$

where r in fiber networks means an equivalent radius of the capillary porous structure, and η is the viscosity of the liquid.

Hence, h^2 values plotted against time show a straight line according to equation (3):

$$h^2 = D \cdot t \tag{3}$$

where the slope D is a capillary diffusion coefficient related to the size of the capillaries r and to the physicochemical characteristics of the liquid. Therefore, a surface treatment of a fabric that modifies r and the contact angle, such as plasma treatment, causes variation of this diffusion coefficient. It was observed that D is affected by the nature of the gas plasma, power, exposure time, and aging. On polyester fabric, nitrogen plasma induces higher wettability than air and oxygen, probably mainly due to surface etching, whereas the wettability of acrylic fabric slightly increases in air plasma with respect to nitrogen.

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3. Water and oil repellency by UV curing

Cotton has always been the principal fiber for clothing fabrics due to its attractive characteristics such as softness, comfort, warmness, biodegradability, and low cost. However, the high concentration of hydroxyl groups on the cotton surface makes the fabric water absorbent and easily stained by liquids. Therefore, additional finishes are required to impart hydrophobicity and self-cleaning properties to cotton fabrics. The same finishes are applied to other fabrics, although based on less hydrophilic fibers such as wool, silk, polyamides, and polyester.

In general, water repellency of a fabric can be defined as the fabric's ability to withstand wetting or penetration by water under test conditions. It is important to distinguish between the terms "water repellent" and "waterproof". A fabric is made water repellent by the surface modification or deposition of hydrophobic material on the fibers. Water repellent fabrics have open pores and are permeable to air and water vapor. They are resistant to wetting by rain drops, water spreading, and wicking. Waterproofing involves filling the pores in the fabric with a material that is impermeable to water and, usually, to air as well. Water-repellent, but not waterproof, fabrics allow passage of water once the hydrostatic pressure is sufficiently high. Waterproof and water-repellent finishes are required, in particular, for cotton fabrics.

Polysiloxanes are widely used for textile finishing to impart desirable properties such as softness, crease resistance, and water repellency. However, the specific properties conferred by siloxanes depend on the nature of organic functional groups that are incorporated in the polymer structure [71]. Moreover, water and oil repellency is required for protective clothes and is currently achieved by thermal polymerization of fluorinated monomers, which enable a strong increase of water and oil contact angles on the treated fabrics [72]. However, the application of a polymeric coating to a cotton fabric in the form of a thin film ensures good homogeneity of the conferred properties, but the fabric could lose comfort characteristics, such as handling and breathability. Therefore, an alternative method that allows the uniform adsorption of monomers onto each fiber and the formation of polymer chains inside the fibers should be preferred, since the interpenetration of components and uniform distribution of monomers, even at a low concentration, contribute to obtaining textile materials with modified surface properties without a high add-on of polymer. This result can be achieved by a radiation curing method.

Radiation processes have several commercial applications for the coating of metals, plastics, and glass in printing, wood finishing, film and plastic crosslinking, and in adhesives and electrical insulations. The advantages of this technology are well known: energy savings (low-temperature process), low environmental impact (no solvent emissions), simple, cheap, small equipment, and high treatment speed. Despite these advantages, there have been few applications of radiation curing in the textile industry, such as nonwoven fabric bonding, fabric coating, pigment printing, silk grafting, and surface modification of cotton and synthetic fibers [73, 74]. In fact, in textile finishing processes, the conventional thermal curing technique is still used, regardless of energy consumption and cost. Among the textile finishing processes by radiation curing, pigment printing of fabrics has received much attention [75], whereas coatings for shrink-resistant wool, flame-retardant fabrics, and durable press finishes have also

been investigated. Recently, studies on the effects of radiations on textile dyeing have been reviewed by Bhatti et al. [76], whereas the application of ultraviolet irradiation to wool dyeing processes has been experimented [24–26].

Water-repellent fabrics have been obtained by γ-radiation grafting of poly(vinyl methyl siloxane) or methyl hydrogen silicone on hydrophilic substrates. In industrial applications, UV light from a mercury vapor lamp is preferred for thin coatings because of its high efficiency of energy absorption and low equipment cost. In UV curing, radical or cationic species are generated by the interaction of UV light with a suitable photoinitiator, which quickly induces the curing reaction of reactive monomers and oligomers at low temperature, with lower environmental impact and lower process cost than the thermal process. If a monomer and photoinitiator mixture is adsorbed onto the fibers and subsequently UV cured, the polymeric chains can form inside the textile structure, which can be also involved in the formation of graft bonds, making the treatment solid and water resistant.

Ferrero et al. [77] proposed the water-repellent finishing of cotton fabrics by radical UV curing of silicone and urethane-acrylates with different formulations. The results of contact angle, wettability, and moisture adsorption showed that water repellency is already significant at a low resin add-on, whereas the treated fabric maintains its own breathability. SEM analysis confirmed that UV curing yields a coating layer onto each single fiber than a film on the fabric surface.

Polyester and nylon fabrics were made superhydrophobic by the UV curing of a polydimethylsiloxane-containing polyurethane oligomer that was synthesized on purpose. The UV-curable system helps the super hydro-repellent polydimethylsiloxane moiety to anchor onto textile surface, improving the washing stability of the treatment [78].

Moreover, photografting as a surface modification method to provide permanent wettability and wicking performance to deep-groove polypropylene fibers was proposed by Zhu and Hirt [79]. In this case, polyacrylamide and polyacrylic acid were grafted on the fibers by UV irradiation; then, the advancing water contact angle on single fibers decreased from 100° to 55°, and spontaneous wicking of water was observed after surface modification.

On the other hand, a number of research papers have been published on the production and application of different types of fluorochemicals for textile finishing. Fluorochemicals are organic compounds consisting of perfluorinated carbon chains with more fluorine than hydrogens attached to carbon, having thermal and chemical stability. These chains, evenly distributed on the fiber with proper orientation, present an essentially fluorinated surface, which imparts water and oil repellency. In fact, the critical surface tension for fluorocarbon surfaces is in the range of 6 mN/m (-CF_3) to 28 mN/m, whereas for bleached cotton, it is 44 mN/m. One of the most successful ways of obtaining this condition is the incorporation of the fluorinated groups into polymer molecules in which perfluoro groups constitute the side chains [80]. The fluorochemicals used nowadays are based on C_6 carbon chains, which have substituted the C_8 fluorocarbons that release perfluorooctanesulfonate and perfluorooctanoic acid, higly hazardous and toxic substances. Selected articles regarding the surface modification of fibers achieved by fluorination are listed in Table 4.

Fiber	Topic	Reference
Wool, cotton, PET	Fluoropolymer latexes coating	Castelvetro 2001 [81]
FR PET, FR rayon	Padding and thermal curing	Shekar 2001 [82]
FR PET, aramid+viscose	Padding and thermal curing	Kasturiya 2003 [83]
Cotton	Perfluoro-alkyl-epoxy	Shao 2004 [84]
Nylon 6	Padding and thermal curing	De 2005 [72]
Nylon 6,6 and PET	Superhydrophobic rough surface	Lee 2007 [85]
Cotton	Crosslinking of perfluorinated acrylate	Li 2008 [86]
Various	Waterproof breathable fabrics	Mukhopadyai 2008 [87]
Cotton, PA, PET	Perfluoro-alkyl-polyacrylates UV-cured	Ferrero 2011 [74]
Cotton	Perfluoro-acrylates UV and thermal cured	Ferrero 2012 [88]
Cotton	Fluorocarbon and sodium CMC	Dhiman 2014 [89]
Cotton	Direct fluorination and polymerization	Maity 2010 [90]
Cotton, PET	Fluorination by SF_6 plasma treatment	Selli 2001 [91]
Cotton	Plasma sputtering	Wi 2010 [92]
Cotton	Thermal, UV curing, plasma	Udrescu 2011 [93]

FR: Flame retardant; PET: polyethyleneterephtalate.

Table 4. Selected articles on the surface modification of textile fibers by fluorination.

Fluorochemical finishings are commercially available as water emulsions and are applied to fabrics by the pad–dry–cure method, i.e., bath impregnation followed by squeezing, drying in air at 80–100 °C, and final curing at 150–175 °C in hot flue for some minutes. Fluorochemicals give water-repellent and soil-release finishes in conjunction with other water repellents, called extenders, which are able to yield fiber coatings with good resistance to washing. Castelvetro et al. [81] studied the performance of fluoropolymer latexes applied by padding to wool, cotton, and polyester fabrics. They evaluated the performances of the fabrics by means of technological standard test methods whose results correlated well with static and dynamic contact angle measurements.

Alternative fluorination methods have been proposed. Maity et al. [90] experimented the direct fluorination of cotton using elemental fluorine and admicellar polymerization, with a surfactant and fluoromonomer system. Selli et al. [91] used a SF6 plasma to confer water and oil repellency to cotton and PET, whereas plasma sputtering was used by Wi et al. to obtain a water-repellent PTFE coating on cotton fibers [92].

On the other hand, Ferrero et al. [88] extended the study of the UV-curing method to the use of perfluoro-alkyl-polyacrylate resins that are able to impart water as well as oil repellency to cotton fabrics, and the results obtained by UV curing were compared with those obtained by conventional thermal polymerization. This study was focused on the use of commercial finishes for thermal application, Repellan EPF and NFC, by Pulcra Chemicals, and Oleophobol CP-C, by Huntsman, supplied in water emulsions (about 17% solid content, dispersible in cold

water in all ratios). Darocur 1173 (2-hydroxy-2-methyl-1-phenylpropan-1-one supplied by Ciba Specialty Chemicals) as a radical photoinitiator was added in an amount of 2% weight on the resin, enough to obtain a film by UV curing with each formulation considered. Water was added as a diluent to the mixtures, continuously stirred until complete homogeneity, in order to enable uniform spread of the liquids on cotton. The formulations were applied by dipping onto strips of fabric that were subsequently dried in an oven. The amount of resin put on the fabrics was adjusted according to the desired final weight add-on and the emulsion concentration. Weight percentages of 3% and 5% on the weight fiber were usually applied in order to obtain the desired properties without loss of fabric handling.

The surface-coated fabrics were exposed to UV radiation using a medium-pressure mercury lamp with a light irradiance on the fabric of about 20 mW/cm^2, in a small box equipped with a quartz window under nitrogen atmosphere, since oxygen interferes with the formation of radicals. The required radiation dose was obtained by adjusting the distance of the textile from the lamp and the exposure time, which was assessed between 40 and 60 s. Instead, thermal curing was carried out in 2–3 min at 140 °C or 150 °C according to the indications of the producer.

Resin emulsion is adsorbed by the fibers, so the polymerized product does not form films onto the fabric surface, but penetrate inside. To test if UV curing was effective even inside the fabric compared with the thermal treatment, the polymerization yield was evaluated by the determination of the unpolymerized resin extracted by chloroform at room temperature from the cured fabrics. Repellan EPF shows the highest yields after UV curing and is about similar to those reached with the thermal treatment (93–96%), whereas Repellan NFC shows lower, although acceptable, yields in UV curing (80–81%) than in the thermal one (98%). With these finishes, the yields remained unaffected by exposure time and resin add-on. Oleophobol CP-C gives lower yields either in thermal or UV curing, with a marked dependence on add-on and exposure time; hence, 60 s is needed to obtain a good yield for a 3% add-on (91%).

The surface properties of coated and uncoated textiles were tested with optical measurements of static and dynamic contact angles of water and oil drops on the textile. The measuring liquids were HPLC grade water (72.8 mN/m at 25 °C) and olive oil (32.0 mN/m). The contact angle values should be higher, as the hydrophobic or oil repellency behavior of the textile is greater. On cotton samples finished with both curing methods, water and oil repellency fastness to domestic washing was evaluated after five washings according to UNI-EN ISO 105-C01.

In Figure 3, the results of dynamic contact angle measurements of water on cotton finished by Repellans before and after washing are compared. In this evaluation, the analysis of advancing and receding contact angles and the resulting difference, i.e. the hysteresis, can give information on the influence of surface roughness and chemical heterogeneity on fabric wettability [81]. A $\Delta\theta>0$ is typical of most real surfaces, as confirmed by all the results obtained. With both resins, the advancing contact angles were slightly reduced after five washing cycles, and this proved the good wash fastness of water repellency, regardless of the curing type and polymer add-on. The hysteresis values generally decreased, indicating a lower surface heterogeneity, probably due to the washing effect. Oleophobol gave slightly lower contact angles but was practically unaffected by repeated washings.

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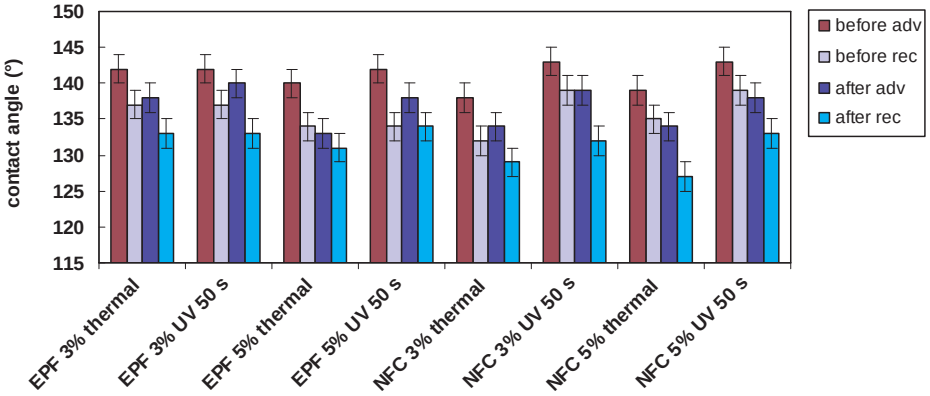

Figure 3. Dynamic contact angles of water before and after washing on cotton fabrics finished with Repellan EPF and NFC (adv: advancing; rec: receding) [with kind permission from Springer Science+Business Media: Ferrero F., Periolatto M., Udrescu C. Water- and oil-repellent coatings of perfluoro-polyacrylate resins on cotton fibers: UV curing in comparison with thermal polymerization. Fibers and Polymers 2012; 13 (2), 191–198, p. 195, Fig. 1].

Static contact angles of oil before and after washing are compared in Figure 4, and the results confirmed the satisfactory wash fastness of oil repellency, in particular with Repellan NFC, without differences between the thermal and UV curing methods.

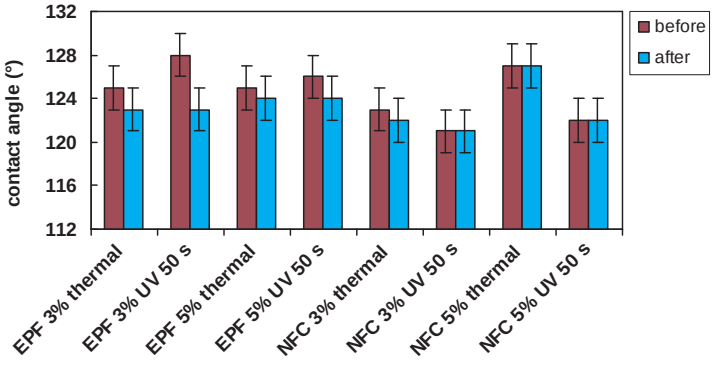

Figure 4. Static contact angles of oil before and after washing on cotton fabrics finished with Repellan EPF and NFC. [with kind permission from Springer Science+Business Media: Ferrero F., Periolatto M., Udrescu C. Water and oil-repellent coatings of perfluoro-polyacrylate resins on cotton fibers: UV curing in comparison with thermal polymerization. Fibers and Polymers 2012; 13(2), 191–198, p. 195, Fig. 2].

The contact angle value on untreated cotton, both with water and oil, was 0° due to the immediate absorption of the drops. It is evident of the high water and oil repellency conferred by the treatment. Measurements on 10 different points of the same sample surface are in good agreement (average values estimated with a confidence interval of ±2° at a 95% confidence level), showing a good uniformity of the coating. The results of thermal and UV curing are

very close and poorly affected by weight gain and UV curing time, suggesting that a low polymer add-on is enough to modify the fiber surface.

With each finishing type, water contact angles are higher than with oil, in agreement with the results reported in the literature with other finishes on cotton [84, 94], although the values are lower than 150°, which is considered the lower limit for super hydrophobic surfaces showing the so-called Lotus effect. However, the UV-cured resins yielded oil contact angles mostly higher than 120°, denoting super oil-repellent surfaces.

X-ray photoelectron spectroscopy (XPS) analysis gives the chemical composition of the fabric surface and provides useful information on the fiber coating. Table 5 shows the relative peak intensities of C_{1s}, O_{1s}, F_{1s}, and Cl_{2p} in XPS measurements of untreated and finished cotton fabrics. For the untreated cotton, only two peaks corresponding to C and O are observed. F_{1s} intensity was found to be about the same for samples that were thermally or UV cured, whereas Repellan NFC showed the lowest values.

Resin	Curing	C_{1s} (%)	O_{1s} (%)	F_{1s} (%)	Cl_{2p} (%)
Untreated cotton	–	60.6	39.4	–	–
Repellan EPF	thermal	42.0	6.1	51.8	–
	UV	43.1	5.7	51.1	–
Repellan NFC	thermal	44.7	10.7	43.3	1.3
	UV	46.0	8.7	43.5	1.7
Oleophobol CP-C	thermal	46.4	7.7	44.7	1.3
	UV	48.0	9.2	41.9	0.9

Table 5. Relative intensities in the XPS spectra of untreated and resin-treated cotton fabrics (3% polymer add-on and 60-s UV curing time).

Information on how fluorine binds to the polymer surface can be obtained from the high-resolution C_{1s} signals. According to Selli et al. [91], the C_{1s} spectrum was resolved into six components corresponding to the groups reported in Table 6 with the relative peak areas. For each resin, small differences arise from the comparison between thermal and UV curing, whereas higher differences can be observed between coatings of the different fluorocarbons. With Oleophobol CP-C, the coatings yielded the lowest percentage of the $–CF_2-$ groups and, conversely, the highest for the –CO- groups, although these differences did not affect water and oil repellency. However, in any case, a much lower concentration of the $–CF_3$ groups was found. Such considerations suggest that the lower content of fluorine groups yielded by Repellan NFC coating is enough to confer the requested surface properties to cotton.

In conclusion, UV curing of cotton with commercial perfluoro-alkyl-polyacrylates applied in water emulsion yielded water- and oil-repellent cotton fabrics like the thermal process. The polymerization yields as well as the contact angles with water and oil were of the same order of those obtained with thermal curing, even at low-resin add-ons. Moreover, the UV-cured resins yielded mostly super oil-repellent surfaces, whereas water and oil repellency was adequately maintained after washing.

Group	Binding energy (eV)	Relative peak area (%)					
		Repellan EPF		Repellan NFC		Oleophobol CP-C	
		Thermal	UV cured	Thermal	UV cured	Thermal	UV cured
-CH-	284.5	35.4	32.1	24.7	30.8	28.9	25.9
-C-O-	285.9	11.1	15.6	37.3	30.5	45.3	41.8
-C=O,-C-CF_x	287.3	-	-	2.9	3.5	5.4	5.0
-COO-,CHF-	288.5	11.9	14.1	8.7	7.7	1.6	7.4
-CF_2-	290.9	37.2	33.3	23.0	24.5	15.8	17.2
-CF_3	293.6	4.4	4.9	3.5	3.1	2.0	2.5

Table 6. High-resolution C_{1s} spectra for resin-treated cotton fabrics (3% polymer add-on and 60-s UV curing time).

XPS analyses showed small differences between thermal and UV-cured coatings with each resin, whereas lower percentages of fluorine groups were observed in the case of Repellan NFC coatings without worsening of water and oil repellency, suggesting that such properties can be obtained with a low polymer add-on (3%) and with the lowest fluorine content.

Therefore, UV curing can be indicated as a valid alternative and environment-friendly method to confer water-resistant hydro and oil repellency to cotton fabrics. A comparison with plasma polymerization on cotton of the same perfluoro-alkyl-polyacrylates [93] confirmed that UV curing yields similar results, but with a simpler apparatus that can easily be introduced in the production lines of continuous fabric finishing.

4. Water and oil repellency by sol–gel techniques

There have been many articles in the literature on the improvement of hydrophobic properties of several kinds of fabrics using nanostructures achieved by nanotechnology. It was demonstrated that superhydrophobicity depends not only on surface chemistry but also on surface topology. Two theoretical models (Wenzel and Cassie–Baxter) have inspired how to engineer superhydrophobic surfaces by either roughening the same through microstructures or nanostructures or lowering the surface-free energy due to waxy materials applied on top of the rough structures, or both. An example is a microprocessing technique for producing rough surface and subsequent chemical treatment with silane- or fluorine-containing polymers to reduce the surface-free energy.

Roughened surfaces have commonly been obtained by the introduction of nano-size particles onto the pristine surface, and the sol–gel technique has been reported as a promising tool for the preparation of water-repellent coatings that is especially versatile for applications on glass, paper, and textile [95–100]. An exhaustive review on the application of sol–gel techniques to textiles has been published by Mahltig and Textor [101], and a series of selected articles is reported in Table 7.

Fiber	Topic	Reference
Nylon, PET/cotton	Hydrorepellency	Mahltig 2003 [102]
Nylon	Finishing of carpeting	Satoh 2004 [103]
Cotton	Superhydrophobicity	Daoud 2004 [104]
Cotton	Superhydrophobicity	Yu 2007 [105]
Wool, cotton, PET	Superhydrophobicity	Wang 2008 [106]
Cotton	Antimicrobial and repellency	Tomšič 2008 [107]
Cotton	Superhydrophobicity	Bae 2009 [108]
Cotton	Superhydrophobicity	Erasmus 2009 [109]
Cotton	Durable hydrophobic finishing	Roe 2009 [110]
Cotton, PET	Hydrorepellency	Gao 2009 [111]
PET, PET/cotton	Hydrorepellency and antistaticity	Textor 2010 [112]
Cotton	Superhydrophobicity	Liu 2011 [113]
Cotton	Water and oil repellency, antimicrobial	Simončič 2012 [114]
Cotton	Superhydrophobicity	Shi 2012 [115]
Cotton	Superhydrophobicity and UV blocking	Pan 2012 [116]
Cotton	Super hydro-oleophobicity, self-cleaning	Vasiljević 2013 [117]
Cotton	Hydrorepellency	Periolatto 2013 [118]
Cotton	Hydrorepellency and oil repellency	Ferrero 2013 [119]
Cotton, PET	Hydrorepellency improved by plasma	Montarsolo 2013 [120]

Table 7. Selected articles on the surface modification of fabrics by sol–gel techniques.

In many research works, sol–gel formulations of fluoroalkylsilanes in combination with other silanes to obtain co-condensates are used. The solvents are mostly alcohols, but some water-based systems have been described. In these nanocomposites, the organic and the inorganic networks are covalently bound and homogeneously intermingled at the nanometer scale so that the resulting coatings show enhanced mechanical stability [96].

These materials have a pronounced gradient structure, with a high concentration of fluoroalkyl groups at the coating–air interface so that only a small amount (1.7 mol%) of fluoroalkyl silane is necessary to obtain an effective repellency. Moreover, it accounts for an excellent adhesion of the coatings on various substrates such as glass, metals, and polymers. The gradient is due to the accumulation of surface-active fluorosilanol molecules and condensates at the interface.

Employing organically modified alkoxysilanes containing long-chained aliphatic or highly fluorinated groups, sol–gel offers far-reaching possibilities to prepare water- as well as oil-repellent textiles. A low required add-on is of great interest for textile applications; in fact, it keeps the typical hand and breathability of fabrics uncompromised. Furthermore, most

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fluorinated materials are very expensive and may often cause serious risks to the human health in case of skin contact and for the environment. Therefore, it is necessary to minimize the use of such substances.

Periolatto et al. [118] obtained highly hydrophobic and oil-repellent cotton fabrics by a one-step deposition of a modified silica-based coatings by sol–gel prepared by co-hydrolysis and condensation in weakly acid medium of TEOS-based sols with low amounts of hydrophobic additives such as hexadecyltrimethoxysilane or fluorooctyltriethoxysilane. This work was further developed [119] with the aim of comparing the effect of the laboratory-grade fluorinated reagent 1H,1H,2H,2H-Fluorooctyltriethoxy-silane (FOS) with that of a commercial product (Fluorolink S10). During the acid-catalyzed hydrolysis of TEOS or fluorinated alkoxysilanes, labile silanol groups are formed, which can first promote the silane adsorption onto the OH-rich cellulose structure of cotton fibers through hydrogen bonding. Successively, during the thermal curing step (120° for 1 h), the condensation reactions reported in Figure 5 can occur.

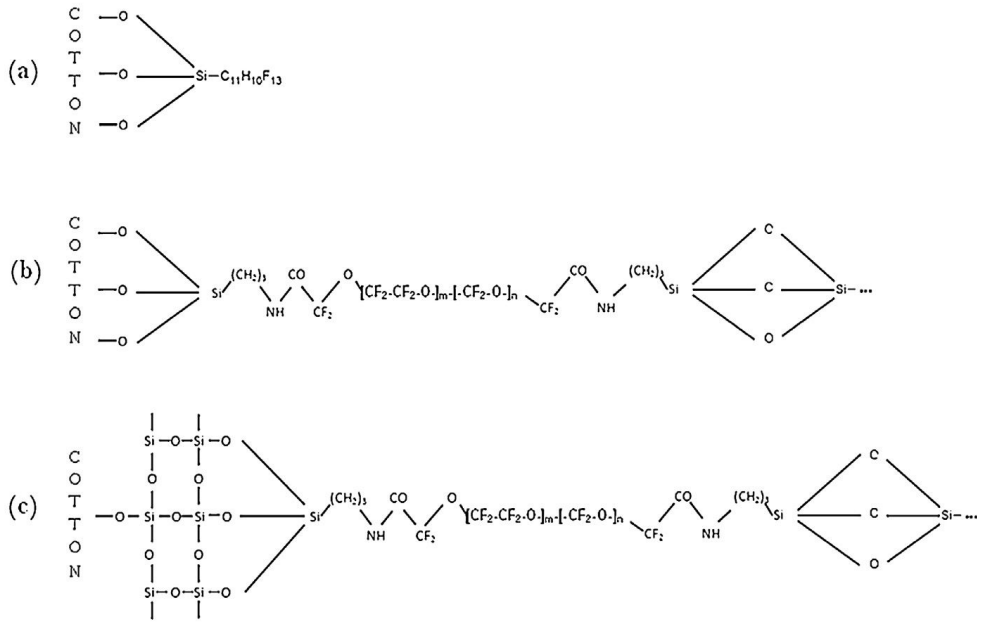

Figure 5. Grafting reactions of fluoromonomers on cotton [reprinted with permission from Elsevier: Ferrero F., Periolatto M. Application of fluorinated compounds to cotton fabrics via sol–gel. Applied Surface Science 2013; 275, 201–207]

The procedure of preparation of the nanosols is illustrated in Figure 6.

The cotton samples were subjected to contact angle measurements by a Krüss DSA20E "Easydrop standard" drop shape analysis tensiometer using the sessile drop method for

fitting. Measuring liquid drops were deposited from a glass syringe on the fabric's surface by means of software-controlled dosing. The contact angles were the average of at least five measurements for each sample, with a standard deviation of about 2–3%. The contact angles on untreated cotton were 0°C, whereas the drops are immediately absorbed. Moreover, the time necessary for the total absorption of both water and oil drops was measured. The results are summarized in Figure 7.

On samples finished with an impregnation time of 24 h, higher values of contact angles were measured (169°), denoting the importance of a deep penetration of the finishing agent inside the fibers.

A better behavior of Fluorolink-treated samples, with respect to the FOS-treated ones, was found: contact angles higher than 150 °C were measured, typical of super hydro- and oil-repellent surfaces. Absorption times higher than 2 h were measured with both water and oil drops, whereas on FOS-treated samples, the oil drop is absorbed in about 15 min, a good result but worse than Fluorolink's performance. This can be due to the molecular structure of Fluorolink, which is longer and more complex than FOS. The presence of TEOS seems to be ineffective.

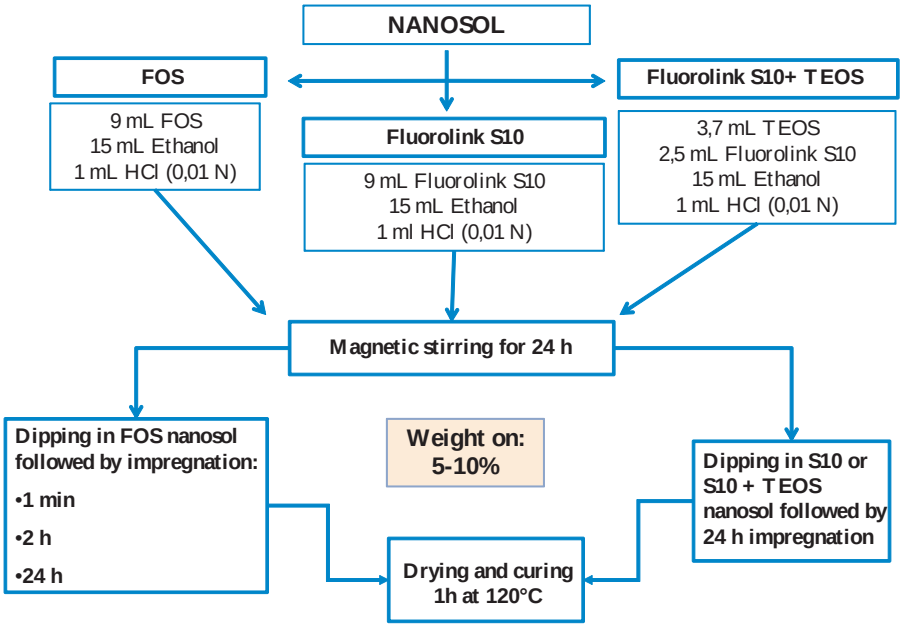

Figure 6. Procedure of sol–gel preparation and its application to cotton fabrics to confer hydro and oil repellency.

The same measurements were made after five repeated washing cycles (at 40 °C for 30 min using 5-g/l ECE detergent according to ISO 105 C01 standard) to assess the durability of the treatments to laundering. The results are summarized in Figure 8.

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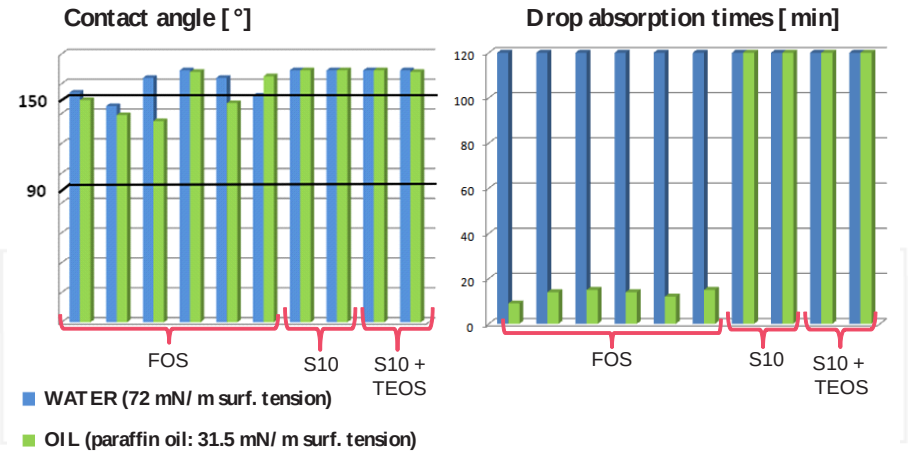

Figure 7. Results of contact angle measurements and drop absorption time on cotton fabrics treated with sol–gel finishes. From left to right; for FOS-finished samples add-on and impregnation time: 5% 1 min, 10% 1 min, 5% 2 h, 10% 2h, 5% 24 h, and 10% 24 h; for the other finishes: 5% 24 h and 10% 24 h.

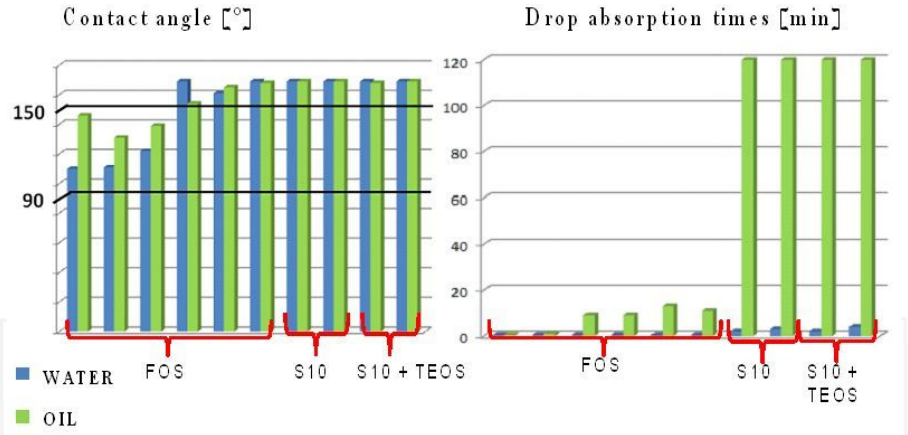

Figure 8. Contact angle and drop absorption time measurements after five washing cycles (description of samples as shown in Figure 7).

On FOS samples after washing, a decrease in contact angles was observed, but the behavior was better with 24 h of impregnation, showing that a longer contact time enables better interpenetration of the finishing agent inside the cotton fibers. Instead, the samples finished by Fluorolink S10 showed the best performance, without the influence of TEOS. After washing, the drop absorption times of water strongly decreased, whereas the oil drop absorption time of 2 h was maintained by samples finished with Fluorolink S10.

The strong loss of hydrophobicity after washing can be due to a rearrangement of the fluorinated chains with an orientation toward the internal part of the fibers. In fact, it is well known that fluorine-containing polymers are usually quite susceptible to rapid rearrangement when the polymer surface is contacted with water, in particular with short perfluorinated-side chains to minimize the interfacial free-energy response to the environmental media. This was confirmed by the increase in contact angle and water drop absorption time of the washed samples after ironing.

The results of XPS analysis confirmed the presence of finishing agents on the surface as evidenced by the content of F and Si. CF_3 groups are present in the structure of FOS, whereas CF_2 groups are present in FOS as well as in Fluorolink. In fact, the F content was higher on the FOS-treated samples (58.3% on the cotton finished with 10% FOS) than that finished with 10% Fluorolink (38.9%). These values were significantly reduced after washing (53.2% and 28.3%, respectively).

In conclusion, the application of a fluorinated alkoxysilane to cotton textiles by sol–gel is a promising textile finishing process to confer durable hydro and oil repellency. In fact, high contact angles and drop absorption time values were measured on treated cotton with both water and oil. Low add-ons (5%) are enough to confer the properties, unaffecting the fabric's characteristics. A prolonged impregnation time (24 h) significantly improves repellency and fastness to washing, whereas ironing of the washed samples can partially restore the hydro and oil repellency lost after washing.

The best performances were obtained with a commercial product (Fluorolink S10). This can allow the application of the treatment at the industrial level, taking into account that the sol–gel process can immediately be implemented on existing production lines of fabric finishing.

5. Conclusions

The modification of surface energy and wettability of textile fibers can be achieved by several techniques, such as plasma treatments, thermal or UV curing of suitable monomers and oligomers, and, finally, nanotechnology based on sol–gel processes.

LPPs are versatile, enabling various treatment types: etching, grafting of groups onto the surface, coating with polymers produced *in situ* from gaseous monomers or liquid oligomers previously impregnated, sputtering, and so on. Despite this flexibility, the apparatus is complex, cumbersome, expensive, and unsuitable for continuous fabric finishing. APP processes are preferable to this aim, but are limited with regard to utilizable gases and plasma polymerization. In any case, the major drawback of plasma activation aimed at improving the following processes is because most of the free radicals remaining on the treated fiber surface is extinguished when exposed to air oxygen; therefore, the time lapse between the plasma treatment and the exploitation of the effects should be as short as possible.

UV curing of suitable monomers or oligomers can be a valid alternative to traditional thermal curing for fabric water and oil repellency and other surface properties. It is a low-cost and environment-friendly process that can easily be introduced in the finishing processes.

Finally, sol–gel processes applied to fabric finishings allow for obtaining engineered surfaces with a great variety of applications arising from the properties of the nanostructures. If low-cost precursors will be found and the need for organic solvents will be reduced to a minimum amount, these techniques will show a significant development in the next years.

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References

[1] Quéré D., Rough ideas on wetting, Physica A 2002 (1–2); 313 32–46.

[2] He B., Lee J., Patankar N. A. Contact angle hysteresis on rough hydrophobic surfaces. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2004; 248 (1–3) 101–104.

[3] Ferrero F., Mossotti R., Innocenti R., Coppa F., Periolatto M. Enzyme-aided wool dyeing: influence of internal lipids. Fibers and Polymers 2015; 16 (2) 363–369.

[4] Holme I. Innovative technologies for high performance textiles. Coloration Technology 2007; 123 59–73.

[5] Kan C. W., Kwon C., Yuen C. W. M. Surface characterization of low temperature plasma treated wool fiber—the effect of the nature of gas. Fibers and Polymers 2004; 5 (1), 52–58.

[6] Kan C. W., Chan K., Yuen C. W. M. Influence of plasma gas on surface composition of low-temperature plasma-treated wool fibre. Indian Journal of Fibre and Textile Research 2005; 30 (1) 60–67.

[7] Kan C. W., Yuen C. W. M., Plasma technology in wool. Textile Progress 2007; 39 (3) 121–187.

[8] Kan C. W. Effect of low temperature plasma on different wool dyeing systems. AUTEX Research Journal 2007; 8 (4) 255–263.

[9] Wang C. X., Qiu Y. P. Two sided modification of wool fabrics by atmospheric pressure plasma jet: influence of processing parameters on plasma penetration. Surface and Coatings Technology 2007; 201 (14) 6273–6277.

[10] Rombaldoni F., Mossotti R., Montarsolo A., Innocenti R., Mazzuchetti G., Vassallo E. Application of HMDSO plasma-aided coating to wool fabrics and characterization of their chemical, surface and physical properties. Proceedings of the 8th AUTEX 2008 Word Textile Conference, 24–26 June, Biella, Italy, CD-ROM version.

[11] Rombaldoni F., Mossotti R., Montarsolo A., Innocenti R., Mazzuchetti G., Vassallo E., Characterization of plasma-coated wool fabrics. Textile Research Journal 2009; 79 (9) 853–861.

[12] Naebe M., Denning R., Huson M., Cookson P. G., Wang X. Ageing effect of plasma-treated wool. Journal of the Textile Institute 2011; 102 (12) 1086–1093.

[13] Riva A., Algaba I., Prieto R. Dyeing kinetics of wool fabrics pretreated with a protease. Coloration Technology 2002; 118 (2) 59–63.

[14] Onar N., Sarıışık M. Use of enzymes and chitosan biopolymer in wool dyeing. Fibers and Textiles in Eastern Europe 2005; 13 (1) 54–59.

[15] Cardamone J. M., Damert W. C. Low-temperature dyeing of wool processed for shrinkage control. Textile Research Journal 2006 (1); 76 78–85.

[16] Parvinzadeh M., Effect of proteolytic enzyme on dyeing of wool with madder. Enzyme and Microbial Technology 2007; 40 (7) 1719–1722.

[17] Cui L., Yu Y., Fan X., Wang P., Wang Q. Effect of protease treatment on dyeing properties of wool fabrics for single bath. Engineering in Life Sciences 2009; 9 (2) 135–139.

[18] Periolatto M., Ferrero F., Giansetti M., Mossotti M., Innocenti R. Enzyme-aided wool dyeing with a neutral protease at reduced temperatures. Engineering in Life Sciences 2010; 10 (5) 474–479.

[19] Periolatto M., Ferrero F., Giansetti M., Mossotti M., Innocenti R. Influence of protease on dyeing of wool with acid dyes. Central European Journal of Chemistry 2011; 9 (1) 157–164.

[20] Shao, J., Liu, J., Carr, C. M. Investigation into the synergistic effect between UV/ozone exposure and peroxide pad—batch bleaching on the printability of wool. Coloration Technology 2001; 117 (5) 270–275.

[21] Xin, J. H., Zhu, R., Hua, J., Shen, J. Surface modification and low temperature dyeing properties of wool treated by UV radiation. Coloration Technology 2002; 118 (4) 169–173.

[22] El-Zaher, N. A., Micheal, M. N. Time optimization of ultraviolet-ozone pretreatment for improving wool fabrics properties. Journal of Applied Polymer Science 2002; 85 (7) 1469–1476.

[23] Micheal, M. N., El-Zaher, N. A. Efficiency of ultraviolet/ozone treatments in the improvement of the dyeability and light fastness of wool. Journal of Applied Polymer Science 2003; 90 (13) 3668–3675.

[24] Periolatto M., Ferrero F., Vineis C., Rombaldoni F. Multifunctional finishing of wool fabrics by chitosan UV-grafting: an approach. Carbohydrate Polymers 2013; 98 (1) 624–629.

[25] Migliavacca G., Ferrero F., Periolatto M. Differential dyeing of wool fabric with metal-complex dyes after ultraviolet irradiation. Coloration Technology 2014; 130 (5) 327–333.

[26] Periolatto M., Ferrero F., Migliavacca G. Low temperature dyeing of wool fabric by acid dye after UV irradiation. The Journal of The Textile Institute 2014; 105 (10) 1058–1064.

[27] Bashar M. M., Khan M. A. An overview on surface modification of cotton fiber for apparel use. Journal of Polymers and the Environment 2013; 21 (1) 181–190.

[28] Enescu D. Use of chitosan in surface modification of textile materials. Romanian Biotechnological Letters 2008; 13 (6) 4037–4048.

[29] Ferrero F., Periolatto M. Antimicrobial finish of textiles of textiles by chitosan UV-curing. Journal of Nanoscience and Nanotechnology 2012; 12 (6) 4803–4810.

[30] Periolatto M., Ferrero F., Vineis C. Antimicrobial chitosan finish of cotton and silk fabrics by UV-curing with 2-hydroxy-2-methylphenylpropane-1-one. Carbohydrate Polymers 2012; 88 (1) 201–205.

[31] Kalia S., Thakur K., Celli A., Kiechel M. A., Schauer C. L. Surface modification of plant fibers using environment friendly methods for their application in polymer composites, textile industry and antimicrobial activities: a review. Journal of Environmental Chemical Engineering 2013; 1 (3) 97–112.

[32] Poll H. U., Schladitz U., Schreiter S. Penetration of plasma effects into textile structures. Surface and Coatings Technology 2001; 142–144 489–483.

[33] Ozdogan E., Saber R., Ayhan H., Seventekin N. A new approach for dyeability of cotton fabrics by different plasma polymerization methods. Coloration Technology 2002; 118 (3) 100–103.

[34] Allan G., Fotheringham A., Weedall P. The use of plasma and neural modeling to optimize the application of a repellent coating to disposable surgical garment. AUTEX Research Journal 2002; 2 (2) 64–68.

[35] McCord M. G., Hwang Y. J., Qiu Y., Hughes L. K., Bourham M. A. Surface analysis of cotton fabrics fluorinated in radio-frequency plasma. Journal of Applied Polymer Science 2003; 88 (8) 2038–2047.

[36] Prabaharan M., Carneiro N. Effect of low-temperature plasma on cotton fabric and its application to bleaching and dyeing. Indian Journal of Fibre and Textile Research 2005; 30 (1) 68–74.

[37] Kim J. H., Liu G., Kim S. H. Deposition of stable hydrophobic coatings with in-line CH_4 atmospheric RF plasma. Journal of Materials Chemistry 2006; 16 (10) 977–981.

[38] Karahan H. A., Ozdoğan E., Demir A., Ayhan H., Seventekin N. Effects of atmospheric plasma treatment on the dyeability of cotton fabrics by acid dyes. Coloration Technology 2008; 124 (2) 106–110.

[39] Pandiyaraj K. N., Selvarajan V. Non-thermal plasma treatment for hydrophilicity improvement of grey cotton fabrics. Journal of Materials Processing Technology 2008; 199 (1–3) 130–139.

[40] Mak C. M., Yuen C. W. M., Ku S. K. A., Kan C. W. Low-temperature plasma treatment of Tencel. Journal of The Textile Institute 2006; 97 (6) 533–540.

[41] El-tahlawy, K. F., El-Bendary, M. A., Elhendawy, A. G., Hudson, S. M. The antimicrobial activity of cotton fabrics treated with different crosslinking agents and chitosan. Carbohydrate Polymers 2005; 60 (4) 421–430.

[42] Alonso, D., Gimeno, M., Olayo, R., Vázquez-Torres, H., Sepúlveda-Sánchez, J. D., Shirai, K. Cross-linking chitosan into UV-irradiated cellulose fibers for the preparation of antimicrobial-finished textiles. Carbohydrate Polymers 2009; 77 (3) 536–543.

[43] Ferrero F., Periolatto M., Ferrario S. Sustainable antimicrobial finishing of cotton fabrics by chitosan UV-grafting: from laboratory experiments to semi industrial scale-up. Journal of Cleaner Production 2015; 96, 244-252.

[44] Negulescu I. I., Despa S., Chen J., Collier B. J., Despa M., Denes A., Sarmadi M., Denes F. S., Characterizing polyester fabrics treated in electrical discharges of radio-frequency plasma. Textile Research Journal 2000; 70 (1) 1–7.

[45] Riccardi C., Barni R., Fontanesi M., Marcandalli B., Massafra M., Selli E., Mazzone G. A SF_6 RF plasma reactor for research on textile treatment. Plasma Sources Science and Technology 2001; 10 (1) 92–98.

[46] Riccardi C., Barni R., Selli E., Mazzone G., Massafra M. R., Marcandalli B., Poletti G. Surface modification of poly(ethylene terephthalate) fibers induced by radio frequency air plasma treatment. Applied Surface Science 2003; 211 (1–4) 386–397.

[47] Barni R., Riccardi C., Selli E., Massafra M. R., Marcandalli B., Orsini F., Poletti G., Meda L. Wettability and dyeability modulation of poly(ethylene terephthalate) fibers through cold SF6 plasma treatment. Plasma Processes and Polymers 2005; 2 (1) 64–72.

[48] Cireli A., Kutlu B., Mutlu M., Surface modification of polyester and polyamide fabrics by low frequency plasma polymerization of acrylic acid. Journal of Applied Polymer Science 2007; 104 (4) 2318–2322.

[49] Calvimontes A., Saha R., Dutschk V. Topological effects of O_2- and NH_3-plasma treatment on woven plain polyester fabric in adjusting hydrophilicity. AUTEX Research Journal 2011; 11 (1) 24–30.

[50] Wang C. X., Liu Y., Xu H. L., Ren Y., Qiu Y. P. Influence of atmospheric pressure plasma treatment time on penetration depth of surface modification into fabric. Applied Surface Science 2008; 254 (8) 2499–2505.

[51] Leroux F., Campagne C., Perwuelz A., Gengembre L. Fluorocarbon nano-coating of polyester fabrics by atmospheric air plasma with aerosol. Applied Surface Science 2008; 254 (13) 3902–3908.

[52] Leroux F., Campagne C., Perwuelz A., Gengembre L., Atmospheric air plasma treatment of polyester textile materials. Textile structure influence on surface oxidation and silicon resin adhesion. Surface and Coatings Technology 2009; 203 (20–21) 3178–3183.

[53] Samanta K. K., Jassal M., Agrawal A., Improvement in water and oil absorbency of textile substrate by atmospheric pressure cold plasma treatment. Surface and Coatings Technology 2009; 203 (10–11) 1336-1342.

[54] Samanta K. K., Jassal M., Agrawal A. K. Antistatic effect of atmospheric pressure glow discharge cold plasma treatment on textile substrates. Fibers and Polymers 2010; 11 (3) 431–437.

[55] Gotoh K., Yasukawa A. Atmospheric pressure plasma modification of polyester fabric for improvement of textile-specific properties. Textile Research Journal 2010; 81 (4) 368–378.

[56] Pane S., Tedesco R., Greger R. Acrylic fabrics treated with plasma for outdoor applications. Journal of Industrial Textiles 2001; 31 (2) 135–145.

[57] Ceria A., Hauser P. J. Atmospheric plasma treatment to improve durability of a water and oil repellent finishing for acrylic fabrics. Surface and Coatings Technology 2010; 204 (9–10) 1535–1541.

[58] Ferrero F. Wettability measurements on plasma treated synthetic fabrics by capillary rise method. Polymer Testing 2003; 22 (5) 571–578.

[59] Ferrero F., Tonin C., Peila R., Ramella Pollone F. Improving the dyeability of synthetic fabrics with basic dyes using in situ plasma polymerization of acrylic acid. Coloration Technology 2004; 120 (1) 30–34.

[60] Kwon Y. A. Influence of the CF_4 plasma treatments on the wettability of polypropylene fabrics. Fibers and Polymers 2002; 3 (4) 174–178.

[61] Väänänen R., Heikkilä P., Tuominen M., Kuusipalo J., Harlin A. Fast and efficient surface treatment for nonwoven materials by atmospheric pressure plasma. AUTEX Research Journal 2010; 10 (1) 8–13.

[62] Shishoo R. (ed.) Plasma Technologies for Textiles. Cambridge: Woodhead Publishing Ltd: 2007.

[63] Radu C. D., Kiekens P., Verschuren J. Surface modification of textiles by plasma treatments. In: Pastore C. M., Kiekens P. (eds.). Surface Characteristics of Fibers and Textiles. New York: Marcel Dekker: 2001. p203–218.

[64] Morent R., De Geyter N., Verschuren J., De Clerk K., Kiekens P., Leys C. Non-thermal plasma treatment of textiles. Surface and Coatings Technology 2008; 202 (14) 3427–3449.

[65] Kale K. H., Desai A. N. Atmospheric pressure plasma treatment of textiles using non-polymerising gases. Indian Journal of Fibre and Textile Research 2011; 36 (3) 289–299.

[66] Wolf R. A. Atmospheric plasma modification of textile surfaces. In: Atmospheric Pressure Plasma for Surface Modification. Somerset: John Wiley & Sons: 2012. p139–154.

[67] Deshmukh R. R., Bhat N. V. Pretreatments of textiles prior to dyeing: plasma processing. In: Hauser P. (ed.). Textile Dyeing. Rijeka: InTech: 2011. p34–56. Available from: http://www.intechopen.com/books/textile-dyeing/pretreatments-of-textiles-prior-to-dyeing-plasma-processing (accessed 10 February 2014).

[68] Hossain M. M., Hegemann D. Substrate independent dyeing of synthetic textiles treated with low-pressure plasmas. In: Hauser P. (ed.). Textile Dyeing. Rijeka: InTech: 2011. p173–194. Available from: http://www.intechopen.com/books/textile-dyeing/substrate-independent-dyeing-of-synthetic-textiles-treated-with-low-pressure-plasmas (accessed 10 February 2014).

[69] Yuan Y., Lee T. R. Contact angle and wetting properties. In: Bracco G., Holst B. (eds.). Surface Science Techniques. Berlin, Heidelberg: Springer-Verlag: 2013. p3–33.

[70] Hegemann D. Plasma Functionalization of Textiles. 2nd ACTECO Training Day 2007, 18 April, Turin, Italy.

[71] El Naggar, A. M.; Zhody, M. H.; Mohammed, S. S.; Alam, E. A. Water resistance and surface morphology of synthetic fabrics covered by polysiloxane/acrylate followed by electron beam irradiation. Nuclear Instruments and Methods in Physics Research B 2003; 201 (4), 595–603.

[72] De P., Sanke M. D., Chaudhari S. S., Mathur M. R. UV-resist, water-repellent breathable fabric as protective textiles. Journal of Industrial Textiles 2005; 34 (4) 209–222.

[73] Ferrero F., Periolatto M., Bianchetto Songia M. Silk grafting with methacrylic and epoxy monomers: thermal process in comparison with ultraviolet curing. Journal of Applied Polymer Science 2008; 110 (2) 1019–1027.

[74] Ferrero F., Periolatto M. Ultraviolet curing for surface modification of textile fabrics. Journal of Nanoscience and Nanotechnology 2011; 11 (10) 8663–8669.

[75] Neral B., Šostar-Turk S., Vončina B. Properties of UV-cured pigment prints on textile fabric. Dyes and Pigments 2006; 68 (2–3) 143–150.

[76] Bhatti I. A., Adeel S., Abbas M. Effect of Radiation in Textile Dyeing. In: Hauser P. (ed.). Textile Dyeing. Rijeka: InTech: 2011. p1–17. Available from: http://www.intechopen.com/books/textile-dyeing/effect-of-radiation-on-textile-dyeing (accessed 10 February 2014).

[77] Ferrero F., Periolatto M., Sangermano M., Bianchetto Songia M. Water-repellent finishing of cotton fabrics by ultraviolet curing. Journal of Applied Polymer Science 2008; 107 (2) 810–818.

[78] Chen W.-H., Chen P.-C., Wang S.-C., Yeh J.-T., Huang C.-Y., Chen K.-N. UV-curable PDMS-containing PU system for hydrophobic textile surface treatment. Journal of Polymer Research 2009; 16 (5) 601–610.

[79] Zhu S., Hirt D.E. Improving the wettability of deep-groove polypropylene fibers by photografting. Textile Research Journal 2009; 79 (6) 534–547.

[80] Kasturiya N., Bhargava G. S. Liquid repellency and durability assessment: a quick technique. Journal of Industrial Textiles 2003; 32 (3) 187–222.

[81] Castelvetro V., Francini G., Ciardelli G., Ceccato M. Evaluating fluorinated acrylic latices as textile water and oil repellent finishes. Textile Research Journal 2001; 71 (5), 399–406.

[82] Shekar R. I., Kasturiya N., Raj H., Mathur G. N. Studies on effect of water repellent treatment on flame retardant properties of fabric. Journal of Industrial Textiles 2001; 30 (3) 222–254.

[83] Kasturiya N., Katiyar P., Bhargava G. S., Nishkam A. Effect of fluorochemicals on flame-retardant fibers. Journal of Industrial Textiles 2003; 32 (4) 245–254.

[84] Shao H., Sun J. Y., Meng W.-D., Qing F.-L. Water and oil repellent and durable press finishes for cotton based on a perfluoroalkyl-containing multi-epoxy compound and citric acid. Textile Research Journal 2004; 74 (10) 851–855.

[85] Lee H. J., Michielsen S. Preparation of a superhydrophobic rough surface. Journal of Polymer Science Part B: Polymer Physics 2007; 45 (3) 253–261.

[86] Li Z.-R., Fu K.-J., Wang L.-J., Liu F. Synthesis of a novel perfluorinated acrylate copolymer containing hydroxyethyl sulfone as crosslinking group and its application on cotton fabrics. Journal of Materials Processing Technology 2008; 205 (1) 243–248.

[87] Mukhopadhyay A., Midha V. K. A review on designing the waterproof breathable fabrics part I: fundamental principles and designing aspects of breathable fabrics. Journal of Industrial Textiles 2008; 37 (3) 225–262.

[88] Ferrero F., Periolatto M., Udrescu C. Water and oil-repellent coatings of perfluoropolyacrylate resins on cotton fibers: UV curing in comparison with thermal polymerization. Fibers and Polymers 2012; 13 (2) 191–198.

[89] Dhiman G., Chakraborty J. N. Soil release performance of cotton finished with oleophobol CPR and CMC–Na salt. Fashion and Textiles 2014; 1 23. Available from: http://link.springer.com/article/10.1186/s40691-014-0023-4

[90] Maity J., Kothary P., O'Rear E. A., Jacob C. Preparation and comparison of hydrophobic cotton fabric obtained by direct fluorination and admicellar polymerization of fluoromonomers. Industrial Engineering Chemistry Research 2010; 49 (13) 6075–6079.

[91] Selli E., Mazzone G., Oliva C., Martini F., Riccardi C., Barni R., Marcandalli B., Massafra M. R. Characterisation of poly(ethylene terephthalate) and cotton fibres after cold SF_6 plasma treatment. Journal of Materials Chemistry 2001; 11 (8) 1985–1991.

[92] Wi D.-Y., Kim I. W., Kim J. Water repellent cotton fabrics prepared by PTFE RF sputtering. Fibers and Polymers 2010; 10 (1) 98–101.

[93] Udrescu C., Periolatto M., Ferrero F. Water-repellent cotton fabrics by ultraviolet curing and plasma treatment. 11th World Textile Conference AUTEX 2011, Mulhouse (France), 8–10 June 2011. p273–276.

[94] Černe L., Simončič B., Željko M. The influence of repellent coatings on surface free energy of glass plate and cotton fabric. Applied Surface Science 2008; 254 (20) 6467–6477.

[95] Latthe S. S., Hirashima H., Rao A. V. TEOS based water repellent silica films obtained by a co-precursor sol–gel method. Smart Materials and Structures 2009; 18 095017 1–6.

[96] Pilotek S., Schmidt H. K. Wettability of microstructured hydrophobic sol–gel coatings. Journal of Sol-Gel Science and Technology 2003; 26 (1–3) 789–792.

[97] Cunha A. G., Gandini A. Turning polysaccharides into hydrophobic materials: a critical review part 1: cellulose. Cellulose 2010; 17 (5) 875–889.

[98] Cappelletto E., Callone E., Campostrini R., Girardi F., Maggini S., della Volpe C., Siboni S., Di Maggio R. Hydrophobic siloxane paper coatings: the effect of increasing methyl substitution. Journal of Sol-Gel Science and Technology 2012; 62 (3) 441–452.

[99] Gowri S., Amorim T., Carneiro N., Souto A. P., Esteves M. F. Polymer nanocomposites for multifunctional finishing of textiles—a review. Textile Research Journal 2010; 80 (13) 1290–1306.

[100] Mahltig B., Haufe H., Bottcher H. Functionalization of textiles by inorganic sol–gel coatings. Journal of Materials Chemistry 2005; 15 (41) 4385–4398.

[101] Textor T., Mahltig B. Nanosols and textiles. Singapore: World Scientific Publishing Co. Pte. Ltd.: 2008.

[102] Mahltig B., Böttcher H. Modified silica sol coatings for water repellent textiles. Journal of Sol-Gel Science and Technology 2003; 27 (1) 43–52.

[103] Satoh K., Nazakumi H., Morita M. Novel fluorinated inorganic–organic finishing materials for nylon carpeting. Textile Research Journal 2004; 74 (12) 1079–1084.

[104] Daoud W. A., Xin J. H., Tao X. Superhydrophobic silica nanocomposite coating by a low-temperature process. Journal of the American Ceramic Society 2004; 87 (9) 1782–1784.

[105] Yu M., Gu G., Meng W.-D., Qing F.-L. Superhydrophobic cotton fabric coating based on a complex layer of silica nanoparticles and perfluorooctylated quaternary ammonium silane coupling agent. Applied Surface Science 2007; 253 (7) 3669–3673.

[106] Wang H., Fang J., Cheng T., Ding J., Qu L., Dai L., Lin T. One-step coating of fluoro-containing silica nanoparticles for universal generation of surface superhydrophobicity. Chemical Communications 2008; 7 877–879.

[107] Tomšič B., Simončič B., Orel B., Černe L., Forte Tavčer P., Zorko M., Jerman I., Vilčnik A., Kovač J. Sol–gel coating of cellulose fibres with antimicrobial and repellent properties. Journal of Sol-Gel Science and Technology 2008; 47 (1) 44–57.

[108] Bae G. Y., Min B. G., Jeong Y. G., Lee S. C., Jang J. H., Koo G. H. Superhydrophobicity of cotton fabrics treated with silica nanoparticles and water-repellent agent. Journal of Colloid and Interface Science 2009; 337 (1) 170–175.

[109] Erasmus E., Barkhuysen F.A. Superhydrophobic cotton by fluorosilane modification. Indian Journal of Fibre and Textile Research 2009; 34(4), 377–379.

[110] Roe B., Zhang X. Durable hydrophobic textile fabric finishing using silica nanoparticles and mixed silanes. Textile Research Journal 2009; 79 (12) 1115–1122.

[111] Gao Q., Zhu Q., Guo Y., Yang C. Q. Formation of highly hydrophobic surfaces on cotton and polyester fabrics using silica sol nanoparticles and nonfluorinated alkylsilane. Industrial Engineering Chemistry Research 2009; 48 (22) 9797–9803.

[112] Textor T., Mahltig B. A sol–gel based surface treatment for preparation of water repellent antistatic textiles. Applied Surface Science 2010; 256 (6) 1668–1674.

[113] Liu J., Huang W., Xing Y., Li R., Dai J. Preparation of durable superhydrophobic surface by sol–gel method with water glass and citric acid. Journal of Sol-Gel Science and Technology 2011; 58 (1) 18–23.

[114] Simončič B., Tomšič B., Cerne L., Orel B., Jerman I., Kovac J., Zerjav M., Simončič A. Multifunctional water and oil repellent and antimicrobial properties of finished cotton: influence of sol–gel finishing procedure. Journal of Sol-Gel Science and Technology 2012; 61 (2) 340–354.

[115] Shi Y., Wang Y., Feng X., Yue G., Yang W. Fabrication of superhydrophobicity on cotton fabric by sol–gel. Applied Surface Science 2012; 258 (20) 8134–8138.

[116] Pan C., Shen L., Shang S., Xing Y. Preparation of superhydrophobic and UV blocking cotton fabric via sol–gel method and self-assembly. Applied Surface Science 2012; 259 110–117.

[117] Vasiljević J., Gorjanc M., Tomšič B., Orel B., Jerman I., Mozetič M., Vesel A., Simončič B. The surface modification of cellulose fibres to create super-hydrophobic, oleophobic and self-cleaning properties. Cellulose 2013; 20 (1) 277–289.

[118] Periolatto M., Ferrero F., Mossotti R., Montarsolo A. Hydrorepellent finishing of cotton fabrics by chemically modified TEOS based nanosol. Cellulose 2013; 20 (1) 355–364.

[119] Ferrero F., Periolatto M., Application of fluorinated compounds to cotton fabrics via sol–gel. Applied Surface Science 2013; 275 201–207.

[120] Montarsolo A., Periolatto M., Zerbola M., Mossotti R., Ferrero F. Hydrophobic sol-gel finishing for textiles: improvement by plasma pre-treatment. Textile Research Journal 2013; 83 (11) 1190–1200.